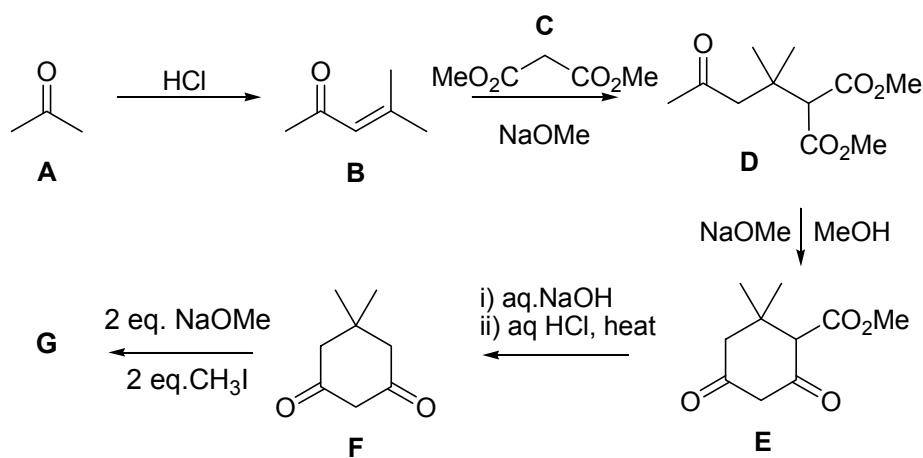
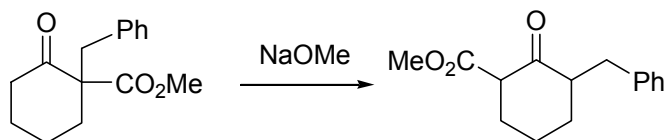


Bifunctional Chemistry, Semester 2, 2007 (06522)

1. Consider the following reaction scheme and answer **all** of the following parts.



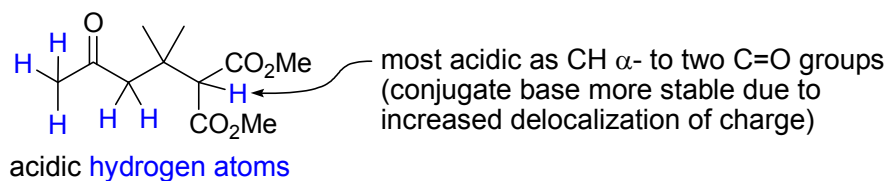
- (a) Identify all the acidic hydrogen atoms in **D** and indicate, with an explanation, which is the most acidic. (4 marks)
- (b) Show how ketone **A** is converted to its enol tautomer under conditions of acid catalysis, and give the mechanism of the reaction which forms **B**. (2,3 marks)
- (c) Dimethyl malonate, **C**, forms an enolate with NaOMe. Give the mechanism of this process and the subsequent conjugate addition to **B** which gives rise to **D**. Why can this reaction be conducted with catalytic amounts of sodium methoxide? (1,3,2 marks)
- (d) What by-product is formed in the conversion of **E** into **F**? Show the mechanism for this reaction. (3 marks)
- (e) Work out the structure of product **G**. (3 marks)
- (f) Propose a mechanism for the reaction below. (4 marks)



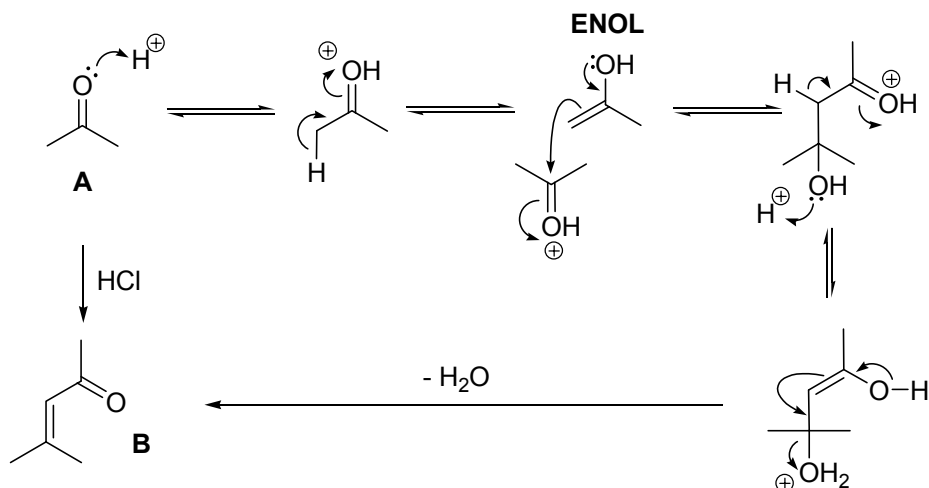
(4 marks)

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MODEL ANSWER

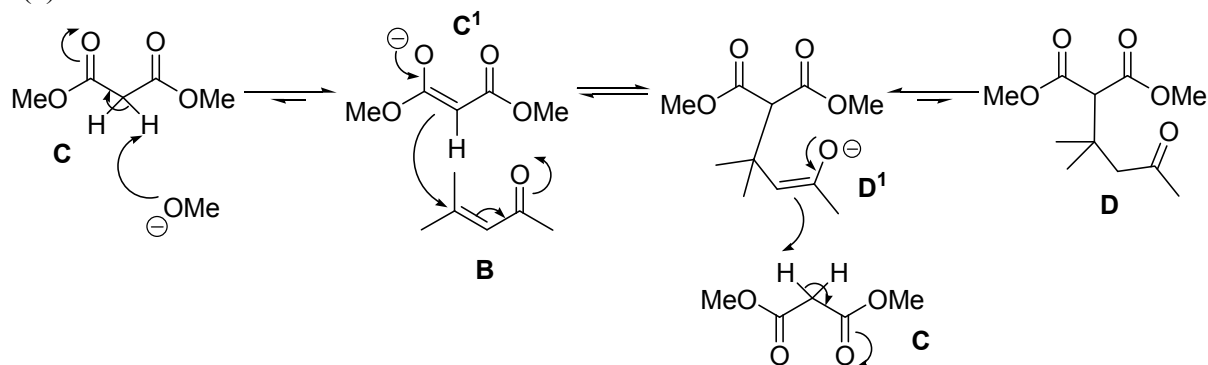
1(a)



1(b)



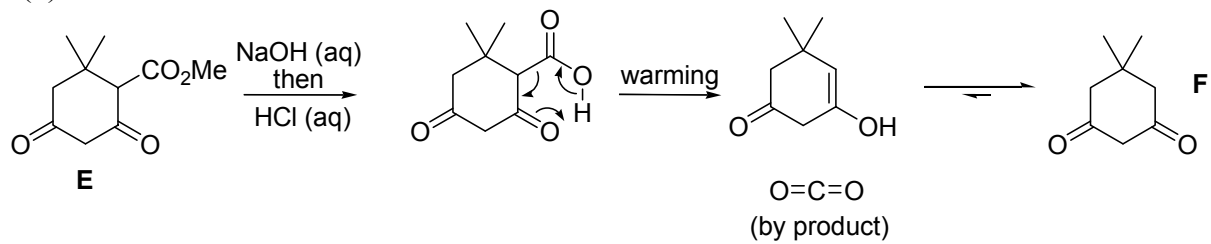
1(c)



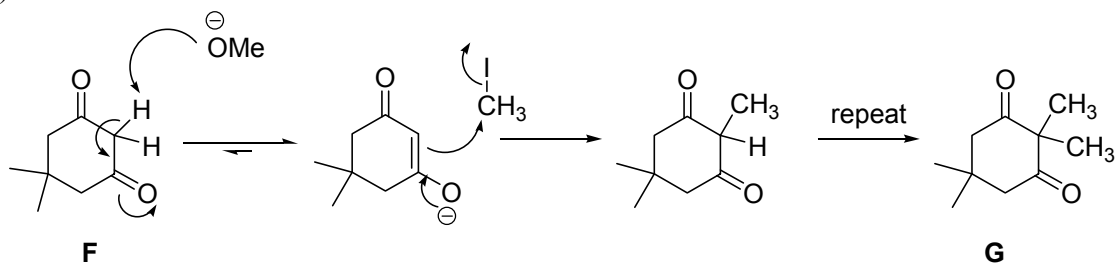
Methoxide deprotonates the malonate **C** (MeOH pKa ~16; dimethyl malonate pKa ~12) producing the enolate **C¹** which then undergoes conjugate addition to the α,β -unsaturated ketone **B** producing enolate **D¹**. This keto enolate, **D¹**, is much more basic than methoxide and so can easily deprotonate **C** and thus perpetuate the cycle. **D¹** may of course also deprotonate the solvent, which of course is present in higher concentration than **C**. E.g. if the reaction is performed in methanol, this would produce more methoxide.

(Also, you may have spotted that there is an acidic α -CH in the malonate portion of the product **D**. If deprotonated however this would make a much less reactive nucleophile due to steric hindrance. This enolate can then easily exchange with unsubstituted dimethyl malonate to keep the reaction going.)

1(d)



1(e)



1(f)

